



(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
09.09.2009 Bulletin 2009/37

(51) Int Cl.:
G03G 5/047 (2006.01) **G03G 5/05** (2006.01)
G03G 5/06 (2006.01) **G03G 5/147** (2006.01)

(21) Application number: **09152422.3**

(22) Date of filing: **10.02.2009**

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA RS

(30) Priority: **04.03.2008 US 42112**

(71) Applicant: **Xerox Corporation**
Rochester, NY 14644 (US)

(72) Inventors:
• **De Jong, Kathy L.**
London Ontario N6H 3K1 (CA)
• **Hu, Nan-Xing**
Oakville Ontario L6H 6B4 (CA)
• **Baranyi, Giuseppa**
Mississauga Ontario L5L 2K3 (CA)

(74) Representative: **Grünecker, Kinkeldey, Stockmair & Schwanhäusser**
Anwaltssozietät
Leopoldstrasse 4
80802 München (DE)

(54) **Self-healing photoconductive member**

(57) Disclosed is a photoconductive member including a self-healing composite coating having a polymer matrix, a photoconductive component, a healing material encapsulated within nano- or microcapsules, and an optional catalyst, that is capable of repairing physical damage to the photoconductive member when the capsule ruptures. Also disclosed is photoconductive member including a substrate, an undercoat layer, a charge generating layer, a charge transport layer, and an optional protective overcoat layer; in which one layer of the photoconductive member further includes a healing material encapsulated within nano- or microcapsules and an optional catalyst, and that is capable of repairing physical damage to the photoconductive member when the capsule ruptures. Also disclosed is an imaging forming apparatus including same.

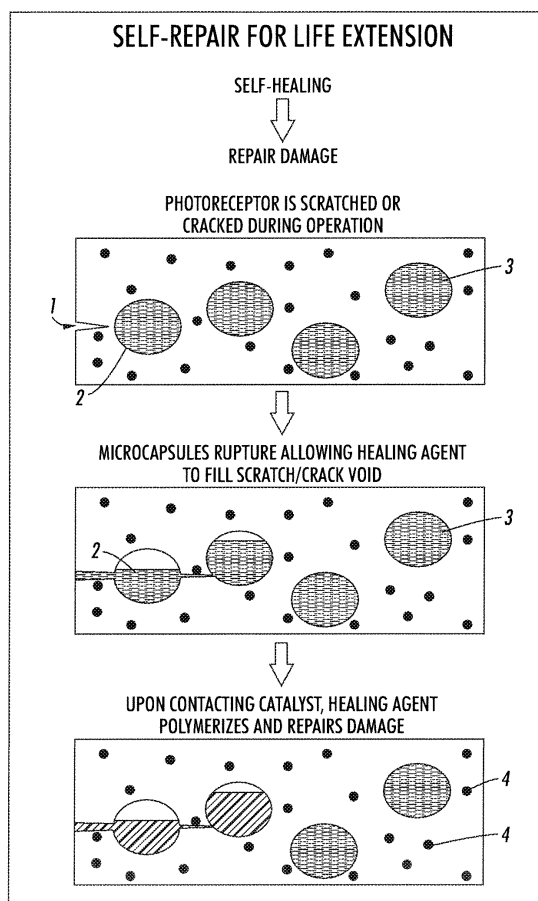


FIG. 1

Description

[0001] This disclosure is generally directed to electrophotographic imaging members and, more specifically, to layered photoreceptor structures comprising a layer composition that is capable of self-healing. This disclosure also relates to processes for making and using the imaging members.

REFERENCES

[0002] U.S. Patent No. 5,702,854 describes an electrophotographic imaging member including a supporting substrate coated with at least a charge generating layer, a charge transport layer and an overcoating layer, said overcoating layer comprising a dihydroxy arylamine dissolved or molecularly dispersed in a crosslinked polyamide matrix. The overcoating layer is formed by crosslinking a crosslinkable coating composition including a polyamide containing methoxy methyl groups attached to amide nitrogen atoms, a crosslinking catalyst and a dihydroxy amine, and heating the coating to crosslink the polyamide. The electrophotographic imaging member may be imaged in a process involving uniformly charging the imaging member, exposing the imaging member with activating radiation in image configuration to form an electrostatic latent image, developing the latent image with toner particles to form a toner image, and transferring the toner image to a receiving member.

[0003] U.S. Patent No. 5,976,744 discloses an electrophotographic imaging member including a supporting substrate coated with at least one photoconductive layer, and an overcoating layer, the overcoating layer including a hydroxy functionalized aromatic diamine and a hydroxy functionalized triarylamine dissolved or molecularly dispersed in a crosslinked acrylated polyamide matrix, the hydroxy functionalized triarylamine being a compound different from the polyhydroxy functionalized aromatic diamine. The overcoating layer is formed by coating.

[0004] U.S. Patent Application Publication No. 2007-0072101 A1, filed September 26, 2005, discloses an electrophotographic imaging member comprising a substrate, a charge generating layer, a charge transport layer, and an overcoating layer, said overcoating layer comprising a cured polyester polyol or cured acrylated polyol film-forming resin and a charge transport material.

[0005] U.S. Patent Application No. 11/295,134 filed December 13, 2005, discloses an electrophotographic imaging member comprising a substrate, a charge generating layer, a charge transport layer, and an overcoating layer, said overcoating layer comprising a terphenyl arylamine dissolved or molecularly dispersed in a polymer binder.

[0006] U.S. Patent Application Publication No. 2006-0105264 A1 filed November 18, 2004, discloses a process for preparing an overcoat for an imaging member, said imaging member comprising a substrate, a charge transport layer, and an overcoat positioned on

said charge transport layer, wherein said process comprises: a) adding and reacting a prepolymer comprising a reactive group selected from the group consisting of hydroxyl, carboxylic acid and amide groups, a melamine formaldehyde crosslinking agent, an acid catalyst, and an alcohol-soluble small molecule to form an overcoat solution; and b) subsequently providing said overcoat solution onto said charge transport layer to form an overcoat layer.

[0007] Phenolic overcoat compositions comprising a phenolic resin and a triarylamine hole transport molecule are known. These phenolic overcoat compositions can be cured to form a crosslinked structure.

[0008] Disclosed in U.S. Pat. No. 4,871,634 is an electrophotographic imaging member containing at least one electrophotoconductive layer. The imaging member comprises a photogenerating material and a hydroxy arylamine compound represented by a certain formula. The hydroxy arylamine compound can be used in an overcoat with the hydroxy arylamine compound bonded to a resin capable of hydrogen bonding such as a polyamide possessing alcohol solubility.

[0009] Disclosed in U.S. Pat. No. 4,457,994 is a layered photosensitive member comprising a generator layer and a transport layer containing a diamine type molecule dispersed in a polymeric binder, and an overcoat containing triphenyl methane molecules dispersed in a polymeric binder.

[0010] The disclosures of each of the foregoing patents are hereby incorporated by reference herein in their entireties. The appropriate components and process aspects of the each of the foregoing patents may also be selected for the present compositions and processes in embodiments thereof.

BACKGROUND

[0011] In electrophotography, also known as Xerography, electrophotographic imaging or electrostatographic imaging, the surface of an electrophotographic plate, drum, belt or the like (imaging member or photoreceptor) containing a photoconductive insulating layer on a conductive layer is first uniformly electrostatically charged. The imaging member is then exposed to a pattern of activating electromagnetic radiation, such as light. The radiation selectively dissipates the charge on the illuminated areas of the photoconductive insulating layer while leaving behind an electrostatic latent image on the non-illuminated areas. This electrostatic latent image may then be developed to form a visible image by depositing finely divided electroscopic marking particles on the surface of the photoconductive insulating layer. The resulting visible image may then be transferred from the imaging member directly or indirectly (such as by a transfer or other member) to a print substrate, such as transparency or paper. The surface of the imaging member is then cleaned by a cleaning unit, such as a cleaning blade, to removal any residual marking particles before next

printing cycle. The imaging process may be repeated many times with reusable imaging members. In order to maintain a clean surface for each print cycle, a cleaning unit, such as a cleaning blade may be incorporated.

[0012] Although excellent toner images may be obtained with multilayered belt or drum photoreceptors, it has been found that as more advanced, higher speed electrophotographic copiers, duplicators, and printers are developed, there is a greater demand on print quality and useful life.. Improved photoreceptor designs must target higher sensitivity, faster discharge, mechanical robustness, and ease of cleaning. The delicate balance in charging image and bias potentials, and characteristics of the toner and/or developer must also be maintained. This places additional constraints on the quality of photoreceptor manufacturing, and thus on the manufacturing yield.

[0013] Imaging members are generally exposed to repetitive electrophotographic cycling, which subjects the exposed charged transport layer, or alternative top layer thereof, to mechanical abrasion, high friction with cleaning blade, and chemical attack from the charging device. This repetitive cycling leads to gradual deterioration in the mechanical and electrical characteristics of the affected layer(s), and often results in the formation of microcracks. In particular, structural polymers are susceptible to the formation of such cracks and/or microcracks, which often form deep within the structure such that detection and repair are impossible. Once such cracks have developed, they significantly and permanently compromise the functionality of the imaging member.

[0014] In conventional photoreceptors, it is mechanical wear due to cleaning blade contact or scratches due to carrier beads or contact with paper that causes photoreceptor devices to fail, and it may not be feasible to continue adding layers to improve photoreceptor robustness. Therefore there is a need to develop new materials and systems that will respond and correct material breakdown as it occurs. Thus, in an effort to extend the life of photoreceptor components to the lifetime of the machine, devices having the ability to respond to their environment are desired. In particular, devices that are self-healing when damage occurs are desired. Such devices would eliminate the need to maintain the machine by either the customer or a technician.

[0015] Despite the various approaches that have been taken for forming imaging members there remains a need for improved imaging member design, to provide improved imaging performance and longer lifetime, reduce its friction with cleaning blade, and minimize the frequency for maintenance, and the like.

SUMMARY

[0016] This disclosure addresses some or all of the above described problems and also provides materials and methods for abrasion wear resistance, reduced friction, and longer lifetime, and the like of electrophoto-

graphic photoreceptors. This is generally accomplished by using a layer composition that is capable of self-healing. Self healing as described herein refers to, for example, the ability of a material to regenerate or repair itself in the event that microcracks, voids, or the like are formed, through a polymerization or repolymerization reaction. In embodiments, self healing materials may be encapsulated in the photoreceptor such that ruptures in the capsules release the healing material. Alternatively, the reactions of multifunctional monomers (e.g. furan and maleimide) that undergo, for example, reverse polymerization reactions, may be incorporated in order to heal damage to the photoreceptor. This disclosure also relates to processes for making and using the imaging members.

[0017] The present invention provides:

(1) A photoconductive member comprised of a self-healing composite coating comprising a polymer matrix, a photoconductive component, a healing material encapsulated within nano- or microcapsules, and an optional catalyst, wherein said healing material is capable of repairing physical damage to the photoconductive member when the capsule ruptures.

(2) The photoconductive member of (1), wherein the nano- or microcapsules comprise at least one of a healing material comprised of a monomer or an oligomer capable of performing polymerization, and a thin wall/shell, wherein said healing material is contained within the wall/shell.

(3) The photoconductive member of (1), wherein said healing material is selected from the group consisting of olefins, cyclic olefins, lactones, acrylates, and organic silanes.

(4) The photoconductive member of (1), wherein said thin wall/shell is comprised of a polymeric material selected from the group consisting of urea-formaldehyde resins, melamine formaldehyde resins, polyesters, and polyurethanes.

(5) The photoconductive member of (1), wherein said catalyst is capable of accelerating the reaction of said healing material, and wherein the catalyst is present in the polymer matrix or on the surface of the capsules.

(6) The photoconductive member of (1), wherein said catalyst comprises at least a member selected from the group consisting of transition metal catalysts, ROMP catalysts, and Lewis acid catalysts.

(7) The photoconductive member of (1), wherein said healing material comprises cyclic olefins, and said catalyst comprises ROMP catalysts.

(8) The photoconductive member of (1), wherein said polymer matrix further possesses a reactive group capable of reacting with the healing material.

(9) The photoconductive member of (8), wherein said reactive group comprises at least a member selected from the group consisting of a vinyl, an acrylic group, a hydrosiloxane group, a diene group, a dielophile

group, and a cyclic olefin group.

(10) The photoconductive member of (8), wherein said reactive group is reacting with the healing material via a chemical reaction selected from the group consisting of metathesis polymerizations, hydrosilations, and Diels-Alder reactions.

(11) The photoconductive member of (1), wherein said photoconductive component is a charge transport compound.

(12) The photoconductive member of (1), wherein said photoconductive component is comprised of a tertiary arylamine.

(13) The photoconductive member of (1), wherein said photoconductive component comprises a photosensitive pigment.

(14) The photoconductive member of (1), wherein said photoconductive component comprises a photosensitive pigment selected from the group consisting of a perylene pigment, an azo pigment, and a phthalocyanine pigment.

(15) The photoconductive member of (1), wherein said photoconductive component is comprised of a semiconductive metal oxide.

(16) The photoconductive member of (1), wherein said polymer matrix is comprised of a member selected from the group consisting of polyesters, polycarbonates, polyethers, polyurethanes, polysiloxanes, polyimides, phenol-formaldehyde resins, melamine-formaldehyde resins, and guamine-formaldehyde resins.

(17) The photoconductive member of (1), wherein said micro-capsules have an average diameter of from about 0.25 micrometer to about 25 micrometers; wherein said nano-capsules have an average diameter of about 20 nanometers to about 250 nanometers.

(18) A photoconductive member comprising a substrate, an undercoat layer, a charge generating layer, a charge transport layer, and an optional protective overcoat layer;

wherein at least one layer of said photoconductive member further comprises a healing material encapsulated within nano- or microcapsules and an optional catalyst,

wherein said healing material is capable of repairing a physical damage of the photoconductive member when the capsule ruptures.

(19) The photoconductive member of (18), wherein said charge generating layer comprises a photosensitive pigment selected from the group consisting of a metal free phthalocyanine, a hydroxygallium phthalocyanine, a chlorogallium phthalocyanine, and a titanium oxide phthalocyanine; said charge transport layer comprises a hole transport compound selected from the group consisting of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, N,N,N',N'-tetra(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,

N'-di-p-tolyl-[p-terphenyl]-4,4"-diamine, and N,N'-bis(4-butylphenyl)-N,N'-di-m-tolyl-[p-terphenyl]-4,4"-diamine; said overcoat layer comprises a crosslinked charge transport composition formed from a reactive charge transport compound comprised of a tertiary arylamine, an optional polyol binder, and a curing agent of a melamine-formaldehyde resin or a guamine-formaldehyde resin; said healing material comprises a monomer or an oligomer capable of performing polymerization.

(20) An imaging forming apparatus comprising a charging device, a toner developer device, a cleaning device, and a photoreceptor comprising a conductive substrate, a charge generating layer, a charge transport layer, and an optional overcoat layer, wherein at least one layer of the photoreceptor contains healing material encapsulated within nano- or microcapsules and an optional catalyst.

[0018] In an embodiment, the present disclosure provides a photoconductive member comprised of a self-healing composite coating comprising a polymer matrix, a photoconductive component, a healing material encapsulated within nano- or microcapsules, and an optional catalyst, wherein said healing material is capable of repairing physical damage to the photoconductive member when the capsule ruptures.

[0019] In another embodiment, the present disclosure provides a photoconductive member comprised of a substrate, an undercoat layer, a charge generating layer, a charge transport layer, and an optional protective overcoat layer;

wherein at least one layer of said photoconductive member further comprises a healing material encapsulated within nano- or microcapsules and an optional catalyst, wherein said healing material is capable of repairing a physical damage of the photoconductive member when the capsule ruptures.

[0020] In another embodiment, the present disclosure provides a photoconductive member comprised of an image forming apparatus comprising a charging device, a toner developer device, a cleaning device, and a photoreceptor comprising a conductive substrate, a charge generating layer, a charge transport layer, and an optional overcoat layer, wherein at least one layer of the photoreceptor contains healing material encapsulated within nano- or microcapsules and an optional catalyst.

[0021] The present disclosure also provides electrophotographic image development devices comprising such electrophotographic imaging members. Also provided are imaging processes using such electrophotographic imaging members.

BRIEF DESCRIPTION OF THE DRAWINGS

[0022] Figure 1 is an illustration of self-healing processes of an Example of the disclosure.

[0023] Figures 2a-2c illustrate further self-healing

processes of Examples of the disclosure.

DETAILED DESCRIPTION

[0024] The present disclosure relates generally to photoconductive imaging members such as photoconductors, photoreceptors and the like, for example that may be used in electrophotographic or xerographic imaging processes. The photoconductive imaging members include at least one layer having a composition that renders the photoreceptor capable of self-healing. Self healing as described herein refers to, for example, the ability of a material to regenerate or repair itself in the event that microcracks, voids, or the like are formed, through a polymerization or repolymerization reaction. Such self healing materials may further be encapsulated whereby the capsules may, in the event of wear or cracking of the photoreceptor, rupture and release the healing material contained within. Additional compounds or catalysts capable of reacting with the self healing materials described herein may also be present, for example, in any layer of the photoreceptor, or in the shell or interior of capsules.

[0025] Electrophotographic imaging members are known in the art. Electrophotographic imaging members may be prepared by any suitable technique. Typically, a flexible or rigid substrate is provided with an electrically conductive surface. A charge generating layer is then applied to the electrically conductive surface. A charge blocking layer may optionally be applied to the electrically conductive surface prior to the application of a charge generating layer. If desired, an adhesive layer may be utilized between the charge blocking layer and the charge generating layer. Usually the charge generation layer is applied onto the blocking layer and a hole or charge transport layer is formed on the charge generation layer, followed by an optional overcoat layer. This structure may have the charge generation layer on top of or below the hole or charge transport layer. In embodiments, the charge generating layer and hole or charge transport layer can be combined into a single active layer that performs both charge generating and hole transport functions.

[0026] The substrate may be opaque or substantially transparent and may comprise any suitable material having the mechanical properties. Accordingly, the substrate may comprise a layer of an electrically non-conductive or conductive material such as an inorganic or an organic composition. As electrically non-conducting materials there may be employed various resins known for this purpose including polyesters, polycarbonates, polyamides, polyurethanes, and the like which are flexible as thin webs. An electrically conducting substrate may be any metal, for example, aluminum, nickel, steel, copper, and the like or a polymeric material, as described above, filled with an electrically conducting substance, such as carbon, metallic powder, and the like or an organic electrically conducting material. The electrically insulating or conductive substrate may be in the form of an endless

flexible belt, a web, a rigid cylinder, a sheet and the like. The thickness of the substrate layer depends on numerous factors, including strength desired and economical considerations. Thus, for a drum, this layer may be of substantial thickness of, for example, up to many centimeters or of a minimum thickness of less than a millimeter. Similarly, a flexible belt may be of substantial thickness, for example, about 250 micrometers, or of minimum thickness less than 50 micrometers, provided there are no adverse effects on the final electrophotographic device.

[0027] In embodiments where the substrate layer is not conductive, the surface thereof may be rendered electrically conductive by an electrically conductive coating. The conductive coating may vary in thickness over substantially wide ranges depending upon the optical transparency, degree of flexibility desired, and economic factors. Accordingly, for a flexible photoresponsive imaging device, the thickness of the conductive coating may be about 20 angstroms to about 750 angstroms, such as about 100 angstroms to about 200 angstroms for an optimum combination of electrical conductivity, flexibility and light transmission. The flexible conductive coating may be an electrically conductive metal layer formed, for example, on the substrate by any suitable coating technique, such as a vacuum depositing technique or electrodeposition. Typical metals include aluminum, zirconium, niobium, tantalum, vanadium and hafnium, titanium, nickel, stainless steel, chromium, tungsten, molybdenum, and the like.

[0028] Illustrative examples of substrates are as illustrated herein, and more specifically layers selected for the imaging members of the present disclosure, and which substrates can be opaque or substantially transparent comprise a layer of insulating material including inorganic or organic polymeric materials, such as MYLAR® a commercially available polymer, MYLAR® containing titanium, a layer of an organic or inorganic material having a semiconductive surface layer, such as indium tin oxide, or aluminum arranged thereon, or a conductive material inclusive of aluminum, chromium, nickel, brass, or the like. The substrate may be flexible, seamless, or rigid, and may have a number of different configurations, such as for example, a plate, a cylindrical drum, a scroll, an endless flexible belt, and the like. In embodiments, the substrate is in the form of a seamless flexible belt. In some situations, it may be desirable to coat on the back of the substrate, particularly when the substrate is a flexible organic polymeric material, an anticurl layer, such as for example polycarbonate materials commercially available as MAKROLON®, a polycarbonate resin having a weight average molecular weight of from about 50,000 to about 100,000, commercially available from Farbenfabriken Bayer A.G., or similar resin.

[0029] The thickness of the photoconductor substrate layer depends on many factors, including economical considerations, electrical characteristics, number of layers, components in each of the layers, and the like, thus

this layer may be of substantial thickness, for example over about 3,000 microns, and more specifically the thickness of this layer can be from about 1,000 to about 3,000 microns, from about 100 to about 1,000 microns or from about 300 to about 700 microns, or of a minimum thickness. In embodiments, the thickness of this layer is from about 75 microns to about 300 microns, or from about 100 to about 150 microns.

[0030] A charge blocking layer or hole blocking layer may optionally be applied to the electrically conductive surface prior to the application of a photogenerating layer. When desired, an adhesive layer may be included between the charge blocking layer, the hole blocking layer or interfacial layer and the photogenerating layer. Usually, the photogenerating layer is applied onto the blocking layer and a charge transport layer or plurality of charge transport layers are formed on the photogenerating layer. This structure may have the photogenerating layer on top of or below the charge transport layer.

[0031] The hole blocking or undercoat layers for the imaging members of the present disclosure can contain a number of components including known hole blocking components. A suitable hole blocking layer may be comprised of polymers such as polyvinyl butyral, epoxy resins, polyesters, polysiloxanes, polyamides, polyurethanes, and the like, nitrogen-containing siloxanes or nitrogen-containing titanium compounds, such as trimethoxysilyl propyl ethylene diamine, N-beta (aminoethyl) gamma-aminopropyl trimethoxy silane, isopropyl 4-aminobenzene sulfonyl titanate, di(dodecylbenzene sulfonyl) titanate, isopropyl di(4-aminobenzoyl) isostearoyl titanate, isopropyl tri(N-ethyl amino) titanate, isopropyl trianthranil titanate, isopropyl tri(N,N-dimethyl-ethyl amino) titanate, titanium-4-amino benzene sulfonate oxyacetate, titanium 4-aminobenzoate isostearate oxyacetate, gamma-aminobutyl methyl dimethoxy silane, gamma-aminopropyl methyl dimethoxy silane, and gamma-aminopropyl trimethoxy silane, for example as disclosed in U.S. Patents No. 4,338,387, 4,286,033 and 4,291,110, each incorporated herein by reference in their entireties.

[0032] The hole blocking layer can also be, for example, comprised of from about 20 weight percent to about 80 weight percent, and more specifically, from about 55 weight percent to about 65 weight percent of a suitable component like a metal oxide, such as TiO_2 , from about 20 weight percent to about 70 weight percent, and more specifically, from about 25 weight percent to about 50 weight percent of a phenolic resin; from about 2 weight percent to about 20 weight percent and, more specifically, from about 5 weight percent to about 15 weight percent of a phenolic compound containing at least two phenolic groups, such as bisphenol S, and from about 2 weight percent to about 15 weight percent, and more specifically, from about 4 weight percent to about 10 weight percent of a plywood suppression dopant, such as SiO_2 . The hole blocking layer coating dispersion can, for example, be prepared as follows. The metal oxide/phenolic resin dis-

persion is first prepared by ball milling or dynamilling until the median particle size of the metal oxide in the dispersion is less than about 10 nanometers, for example from about 5 to about 9. To the above dispersion are added a phenolic compound and dopant followed by mixing. The hole blocking layer coating dispersion can be applied by dip coating or web coating, and the layer can be thermally cured after coating. The hole blocking layer resulting is, for example, of a thickness of from about 0.01 micron to about 30 microns, and more specifically, from about 0.1 micron to about 8 microns. Examples of phenolic resins include formaldehyde polymers with phenol, *p*-tert-butylphenol, cresol, such as VARCUM™ 29159 and 29101 (available from OxyChem Company), and DURITE™ 97 (available from Borden Chemical); formaldehyde polymers with ammonia, cresol and phenol, such as VARCUM™ 29112 (available from OxyChem Company); formaldehyde polymers with 4,4'-(1-methylethylidene)bisphenol, such as VARCUM™ 29108 and 29116 (available from OxyChem Company); formaldehyde polymers with cresol and phenol, such as VARCUM™ 29457 (available from OxyChem Company), DURITE™ SD-423A, SD-422A (available from Borden Chemical); or formaldehyde polymers with phenol and *p*-tert-butylphenol, such as DURITE™ ESD 556C (available from Border Chemical).

[0033] The optional hole blocking layer may be applied to the substrate. Any suitable and conventional blocking layer capable of forming an electronic barrier to holes between the adjacent photoconductive layer (or electrophotographic imaging layer) and the underlying conductive surface of substrate may be selected.

[0034] The optional hole blocking or undercoat layers for the imaging members of the present disclosure can contain a number of components including known hole blocking components, such as amino silanes, doped metal oxides, a metal oxide like titanium, chromium, zinc, tin and the like; a mixture of phenolic compounds and a phenolic resin or a mixture of two phenolic resins, and optionally a dopant such as SiO_2 . The phenolic compounds usually contain at least two phenol groups, such as bisphenol A (4,4'-isopropylidenediphenol), E (4,4'-ethylidenebisphenol), F (bis(4-hydroxyphenyl)methane), M (4,4'-(1,3-phenylenediisopropylidene)bisphenol), P (4,4'-(1,4-phenylene diisopropylidene)bisphenol), S (4,4'-sulfonyldiphenol), and Z (4,4'-cyclohexylidenebisphenol); hexafluorobisphenol A (4,4'-(hexafluoro isopropylidene) diphenol), resorcinol, hydroxyquinone, catechin, and the like.

[0035] In embodiments, a suitable known adhesive layer can be included in the photoconductor. Typical adhesive layer materials include, for example, polyesters, polyurethanes, and the like. The adhesive layer thickness can vary and in embodiments is, for example, from about 0.05 micrometer (500 Angstroms) to about 0.3 micrometer (3,000 Angstroms). The adhesive layer can be deposited on the hole blocking layer by spraying, dip coating, roll coating, wire wound rod coating, gravure coating,

Bird applicator coating, and the like. Drying of the deposited coating may be effected by, for example, oven drying, infrared radiation drying, air drying and the like.

[0036] As optional adhesive layers usually in contact with or situated between the hole blocking layer and the photogenerating layer, there can be selected various known substances inclusive of copolyesters, polyamides, poly(vinyl butyral), poly(vinyl alcohol), polyurethane and polyacrylonitrile. This layer is, for example, of a thickness of from about 0.001 micron to about 1 micron, or from about 0.1 to about 0.5 micron. Optionally, this layer may contain effective suitable amounts, for example from about 1 to about 10 weight percent, of conductive and nonconductive particles, such as zinc oxide, titanium dioxide, silicon nitride, carbon black, and the like, to provide, for example, in embodiments of the present disclosure further desirable electrical and optical properties.

[0037] The photogenerating layer in embodiments is comprised of, for example, about 60 weight percent of Type V hydroxygallium phthalocyanine or chlorogallium phthalocyanine, and about 40 weight percent of a resin binder like poly (vinyl chloride-co-vinyl acetate) copolymer, such as VMCH (available from Dow Chemical). Generally, the photogenerating layer can contain known photogenerating pigments, such as metal phthalocyanines, metal free phthalocyanines, alkylhydroxyl gallium phthalocyanines, hydroxygallium phthalocyanines, chlorogallium phthalocyanines, perylenes, especially bis (benzimidazo)perylene, titanyl phthalocyanines, and the like, and more specifically, vanadyl phthalocyanines, Type V hydroxygallium phthalocyanines, and inorganic components such as selenium, selenium alloys, and trigonal selenium. The photogenerating pigment can be dispersed in a resin binder similar to the resin binders selected for the charge transport layer, or alternatively no resin binder need be present. Generally, the thickness of the photogenerating layer depends on a number of factors, including the thicknesses of the other layers and the amount of photogenerating material contained in the photogenerating layer. Accordingly, this layer can be of a thickness of, for example, from about 0.05 micron to about 10 microns, and more specifically, from about 0.25 micron to about 2 microns when, for example, the photogenerating compositions are present in an amount of from about 30 to about 75 percent by volume. The maximum thickness of this layer in embodiments is dependent primarily upon factors, such as photosensitivity, electrical properties and mechanical considerations. The photogenerating layer binder resin is present in various suitable amounts, for example from about 1 to about 50, and more specifically, from about 1 to about 10 weight percent, and which resin may be selected from a number of known polymers, such as poly(vinyl butyral), poly(vinyl carbazole), polyesters, polycarbonates, poly(vinyl chloride), polyacrylates and methacrylates, copolymers of vinyl chloride and vinyl acetate, phenolic resins, polyurethanes, poly(vinyl alcohol), polyacrylonitrile, polysty-

rene, and the like. It is desirable to select a coating solvent that does not substantially disturb or adversely affect the other previously coated layers of the device. Examples of coating solvents for the photogenerating layer are ketones, alcohols, aromatic hydrocarbons, halogenated aliphatic hydrocarbons, ethers, amines, amides, esters, and the like. Specific solvent examples are cyclohexanone, acetone, methyl ethyl ketone, methanol, ethanol, butanol, amyl alcohol, toluene, xylene, chlorobenzene, carbon tetrachloride, chloroform, methylene chloride, trichloroethylene, tetrahydrofuran, dioxane, diethyl ether, dimethyl formamide, dimethyl acetamide, butyl acetate, ethyl acetate, methoxyethyl acetate, and the like.

[0038] The photogenerating layer may comprise amorphous films of selenium and alloys of selenium and arsenic, tellurium, germanium and the like, hydrogenated amorphous silicon and compounds of silicon and germanium, carbon, oxygen, nitrogen and the like fabricated by vacuum evaporation or deposition. The photogenerating layers may also comprise inorganic pigments of crystalline selenium and its alloys; Group II to VI compounds; and organic pigments such as quinacridones, polycyclic pigments such as dibromo anthanthrone pigments, perylene and perinone diamines, polynuclear aromatic quinones, azo pigments including bis-, tris- and tetrakis-azos; and the like dispersed in a film forming polymeric binder and fabricated by solvent coating techniques; and a number of phthalocyanines, like a titanyl phthalocyanine, titanyl phthalocyanine Type V; oxyvanadium phthalocyanine, chloroaluminum phthalocyanine, copper phthalocyanine, oxytitanium phthalocyanine, chlorogallium phthalocyanine, hydroxygallium phthalocyanine magnesium phthalocyanine and metal free phthalocyanine and the like with infrared sensitivity photoreceptors exposed to low-cost semiconductor laser diode light exposure devices.

[0039] In embodiments, examples of polymeric binder materials that can be selected as the matrix for the photogenerating layer are illustrated in U.S. Patent 3,121,006, the disclosure of which is totally incorporated herein by reference. Examples of binders are thermoplastic and thermosetting resins, such as polycarbonates, polyesters, polyamides, polyurethanes, polystyrenes, polyarylethers, polyarylsulfones, polybutadienes, polysulfones, polyethersulfones, polyethylenes, polypropylenes, polyimides, polymethylpentenes, poly (phenylene sulfides), poly(vinyl acetate), polysiloxanes, polyacrylates, polyvinyl acetals, polyamides, polyimides, amino resins, phenylene oxide resins, terephthalic acid resins, phenoxy resins, epoxy resins, phenolic resins, polystyrene and acrylonitrile copolymers, poly(vinyl chloride), vinyl chloride and vinyl acetate copolymers, acrylate copolymers, alkyd resins, cellulosic film formers, poly(amideimide), styrenebutadiene copolymers, vinylidene chloride-vinyl chloride copolymers, vinyl acetate-vinylidene chloride copolymers, styrene-alkyd resins, poly(vinyl carbazole), and the like. These polymers may be block, random or alternating copolymers.

[0040] The coating of the photogenerating layer in embodiments of the present disclosure can be accomplished with spray, dip or wire-bar methods such that the final dry thickness of the photogenerating layer is as illustrated herein, and can be, for example, from about 0.01 to about 30 microns after being dried at, for example, about 40°C to about 150°C for about 15 to about 90 minutes. More specifically, photogenerating layer of a thickness, for example, of from about 0.1 to about 30, or from about 0.5 to about 2 microns can be applied to or deposited on the substrate, on other surfaces in between the substrate and the charge transport layer, and the like. The photogenerating composition or pigment is present in the resinous binder composition in various amounts. From about 5 percent by volume to about 90 percent by volume of the photogenerating pigment is dispersed in about 10 percent by volume to about 95 percent by volume of the resinous binder, or from about 20 percent by volume to about 30 percent by volume of the photogenerating pigment is dispersed in about 70 percent by volume to about 80 percent by volume of the resinous binder composition. In one embodiment, about 10 percent by volume of the photogenerating pigment is dispersed in about 90 percent by volume of the resinous binder composition.

[0041] Various suitable and conventional known processes may be used to mix, and thereafter apply the photogenerating layer coating mixture, like spraying, dip coating, roll coating, wire wound rod coating, vacuum sublimation, and the like. For some applications, the photogenerating layer may be fabricated in a dot or line pattern. Removal of the solvent of a solvent-coated layer may be effected by any known conventional techniques such as oven drying, infrared radiation drying, air-drying and the like.

[0042] In embodiments, at least one charge transport layer is comprised of at least one hole transport component. The concentration of the hole transport component may be low to, for example, achieve increased mechanical strength and LCM resistance in the photoconductor. In embodiments the concentration of the hole transport component in the charge transport layer may be from about 10 weight percent to about 65 weight percent and more specifically from about 35 to about 60 weight percent, or from about 45 to about 55 weight percent.

[0043] The charge transport layer, such layer being generally of a thickness of from about 5 microns to about 90 microns, and more specifically, of a thickness of from about 10 microns to about 40 microns, may include a number of hole transport compounds, such as substituted aryl diamines and known hole transport molecules, as illustrated herein, and additional components, including additives, such as antioxidants, a number of polymer binders and the like. In embodiments, additives may include at least one additional binder polymer, such as from 1 to about 5 polymers in a percent weight range of about 10 to about 75 in the charge transport layer; at least one additional hole transport molecule, such as from 1 to

about 7, 1 to about 4, or from 1 to about 2 in a percent weight range of about 10 to about 75 in the charge transport layer; antioxidants; like IRGONAX (available from Ciba Specialty Chemical), in a percent weight range of about 0 to about 20, from about 1 to about 10, or from about 3 to about 8 weight percent.

[0044] The charge transport layer may comprise hole transporting small molecules dissolved or molecularly dispersed in a film forming electrically inert polymer such as a polycarbonate. In embodiments, "dissolved" refers, for example, to forming a solution in which the small molecule is dissolved in the polymer to form a homogeneous phase; and "molecularly dispersed in embodiments" refers, for example, to hole transporting molecules dispersed in the polymer, the small molecules being dispersed in the polymer on a molecular scale. Various hole transporting or electrically active small molecules may be selected for the charge transport layer. In embodiments, hole transport refers, for example, to hole transporting molecules as a monomer that allows the free charge generated in the photogenerating layer to be transported across the transport layer.

[0045] Examples of hole transporting molecules include, for example, pyrazolines such as 1-phenyl-3-(4'-diethylamino styryl)-5-(4"-diethylamino phenyl)pyrazoline; aryl amines such as N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-di-p-tolyl-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-di-m-tolyl-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-di-o-tolyl-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-bis(4-isopropylphenyl)-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-bis(2-ethyl-6-methylphenyl)-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-bis(2,5-dimethylphenyl)-[p-terphenyl]-4,4'-diamine, N,N'-diphenyl-N,N'-bis(3-chlorophenyl)-[p-terphenyl]-4,4'-diamine; hydrazones such as N-phenyl-N-methyl-3-(9-ethyl)carbazyl hydrazone and 4-diethyl amino benzaldehyde-1,2-diphenyl hydrazone; and oxadiazoles such as 2,5-bis(4-N,N'-diethylaminophenyl)-1,2,4-oxadiazole, stilbenes, and the like. However, in embodiments to minimize or avoid cycle-up in equipment, such as printers, with high throughput, the charge transport layer should be substantially free (less than about two percent) of di or triamino-triphenyl methane. A small molecule charge transporting compound that permits injection of holes into the photogenerating layer with high efficiency and transports them across the charge transport layer with short transit times includes N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-di-p-tolyl-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-di-m-tolyl-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-di-o-tolyl-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-bis(4-isopropylphenyl)-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-bis(2-ethyl-6-methylphenyl)-[p-terphenyl]-4,4'-diamine, N,N'-bis(4-butylphenyl)-N,N'-bis(2,5-dimethylphenyl)-[p-terphenyl]-4,4'-diamine,

and N,N'-diphenyl-N,N'-bis(3-chlorophenyl)-[p-terphenyl]-4,4''-diamine, tetra[p-tolyl] biphenyldiamine also referred to as N,N,N',N'-tetra(4-methylphenyl)-(1,1'-biphenyl)-4,4'-diamine; N,N,N',N'-tetra(4-ethylphenyl)-(1,1'-biphenyl)-4,4'-diamine; N,N,N',N'-tetra(4-propylphenyl)-(1,1'-biphenyl)-4,4'-diamine; N,N,N',N'-tetra(4-butylphenyl)-(1,1'-biphenyl)-4,4'-diamine, or mixtures thereof, and the like. If desired, the hole transport material in the charge transport layer may comprise a polymeric hole transport material or a combination of a small molecule hole transport material and a polymeric hole transport material.

[0046] Examples of the binder materials selected for the charge transport layer include components, such as those described in U.S. Patent 3,121,006, the entire disclosure of which is totally incorporated herein by reference. Specific examples of polymer binder materials include polycarbonates, polyarylates, acrylate polymers, vinyl polymers, cellulose polymers, polyesters, polysiloxanes, polyamides, polyurethanes, poly(cyclo olefins), epoxies, and random or alternating copolymers thereof; and more specifically, polycarbonates such as poly(4,4'-isopropylidene-diphenylene)carbonate (also referred to as bisphenol-A-polycarbonate), poly(4,4'-cyclohexylidenediphenylene)carbonate (also referred to as bisphenol-Z-polycarbonate), poly(4,4'-isopropylidene-3,3'-dimethyl-diphenyl) carbonate (also referred to as bisphenol-C-polycarbonate), and the like. In embodiments, electrically inactive binders are comprised of polycarbonate resins with a molecular weight of from about 20,000 to about 100,000, such as a molecular weight M_w of from about 50,000 to about 100,000. Generally, the transport layer contains from about 10 to about 75 percent by weight of the hole transport material, and more specifically, from about 35 percent to about 50 percent of this material.

[0047] The thickness of the charge transport layer in embodiments is from about 5 to about 90 micrometers, but thicknesses outside this range may in embodiments also be selected. The charge transport layer should be an insulator to the extent that an electrostatic charge placed on the hole transport layer is not conducted in the absence of illumination at a rate sufficient to prevent formation and retention of an electrostatic latent image thereon. In general, the ratio of the thickness of the charge transport layer to the photogenerating layer can be from about 2:1 to 200:1, and in some instances 400:1. The charge transport layer is substantially nonabsorbing to visible light or radiation in the region of intended use, but is electrically "active" in that it allows the injection of photogenerated holes from the photoconductive layer, or photogenerating layer, and allows these holes to be transported through itself to selectively discharge a surface charge on the surface of the active layer.

[0048] A number of processes may be used to mix and thereafter apply the charge transport layer coating mixture to the photogenerating layer. Typical application techniques include spraying, dip coating, roll coating,

wire wound rod coating, and the like. Drying of the charge transport deposited coating may be effected by any suitable conventional technique such as oven drying, infrared radiation drying, air drying, and the like.

[0049] An overcoat layer may be formed over the charge transport layer. This protective overcoat layer may increase the extrinsic life of a photoreceptor device and may maintain good printing quality or deletion resistance when used in an image forming apparatus.

[0050] The overcoat layer may comprise the same components as the charge transport layer wherein the weight ratio between the charge transporting small molecule and the suitable electrically inactive resin binder is less, such as for example, from about 0/100 to about 60/40, or from about 20/80 to about 40/60.

[0051] Alternatively, a protective overcoat layer comprises a crosslinked polymer coating containing a charge transport component. Specific examples of overcoat layer comprise crosslinked polymer coatings formed from polysiloxanes, phenolic resins, melamine resins and the like, with a suitable charge transport component. An illustrative example of protective overcoats, such as U.S. Patent Application No. 11/234,275 (filed September 26, 2005), may include a cured composition formed from (i) a polyol binder, (ii) a melamine-formaldehyde curing agent; (iii) a hole transport material; and (iv) an acid catalyst.

[0052] The thickness of the overcoat layer selected depends upon the abrasiveness of the charging (bias charging roll), cleaning (blade or web), development (brush), transfer (bias transfer roll), and the like in the system employed, and can be continuous and may have a thickness of less than about 50 micrometers, for example from about 0.1 micrometers to about 50 micrometers, for example from about 0.1 micrometers to about 15 micrometers. Various suitable and conventional methods may be used to mix, and thereafter apply the overcoat layer coating mixture to the photogenerating layer. Typical application techniques include spraying, dip coating, roll coating, wire wound rod coating, and the like. Drying of the deposited coating may be effected by any suitable conventional technique, such as oven drying, infrared radiation drying, air drying, and the like. The dried overcoating layer of this disclosure should transport holes during imaging and should not have too high a free carrier concentration. Free carrier concentration in the overcoat increases the dark decay.

[0053] In embodiments, any layer of the photoreceptor may comprise materials for self-healing. Self healing as described herein refers to, for example, the ability of a material to regenerate or repair itself in the event that microcracks, voids, or the like are formed, through a polymerization or repolymerization reaction. Self-healing materials and properties are beneficial in that damage can be mitigated or repaired whether it occurs by direct contact, e.g. wear caused by cleaning blades such as with drum photoreceptors; or by indirect means, such as cracking in belt photoreceptors. For example, microc-

racks are often precursors to structural failure. Thus, repairing microcracks as they begin to form will extend the life of the photoreceptor and reduce costs associated with parts and maintenance. Devices and methods that include self healing materials are highly advantageous in extending the life of the photoreceptor, improving image quality, and reducing the need for maintenance. In embodiments, the self-healing materials may thus exhibit long shelf life, low monomer viscosity and volatility, rapid polymerization at ambient conditions, and low shrinkage upon polymerization.

[0054] Any suitable material may be incorporated into the desired layer of the photoreceptor to provide self-healing capabilities. Such materials may thereby provide the layer with the ability to self-heal, for example, upon formation of micro-cracks or the like. For example, the undercoat layer may comprise a healing material; the charge generating layer may comprise a healing material; the charge transport layer may comprise a healing material; or the protective overcoat layer may comprise a healing material. Suitable healing materials include monomers, oligomers, or prepolymers, which are capable of forming a polymer to repair mechanical damages such as cracks. To avoid adverse impact on the performance of the photoconductive later, such as mechanical strength or photoconductive properties, the healing materials described herein are typically contained within nano- or micro-capsules. The capsules filled with liquid healing materials are dispersed in the photoconductive composite layer. When a crack forms in the photoconductive coating, for instance, some of the capsules rupture, and deliver the healing materials to repair the crack by forming a polymer. To facilitate the healing process, an initiator or a catalyst may be included to activate or accelerate the polymerization of the healing materials. The catalyst may be distributed within the entire photoconductive coating. In another manner, the catalyst can be embedded on the surface of the capsules.

[0055] In embodiments, any layer of the photoreceptor may comprise a self-healing material that is encapsulated in microcapsules. For example, the charge generating layer may comprise a self-healing material that is encapsulated in nano-or microcapsules; the charge transport layer may comprise a self-healing material that is encapsulated in nano-or microcapsules; or the protective overcoat layer may comprise a self-healing material that is encapsulated in nano-or microcapsules. Nano-or microcapsules not only store the self-healing material during quiescent states, but provide a mechanical trigger for the self-healing process when damage occurs in the host material and the capsules rupture. For example, as seen in the Figure, in the event of wear or cracking of the photoreceptor 1, the capsules 3 may be forced to rupture, thereby releasing the self-healing material 2. Optionally, a catalyst 4 may also be present within a microcapsule 3 or embedded directly into a layer of the photoreceptor 1. The rupturing may occur, for example, by direct contact of exposed microcapsules on the surface layer with a

cleaning blade or other conventional component of a development apparatus, or by stress rupture when cracks occur. Such self-healing material will reduce the wear that would otherwise damage the photoreceptor.

[0056] Optionally, a catalyst or other compound capable of reacting with the self healing materials may also be present. Such a catalyst or other compound may be, for example, embedded in a layer of the photoreceptor, embedded on the surface of the capsule, or encapsulated in nano- or microcapsules. In embodiments, when the photoreceptor becomes cracked, the capsules may thus be designed to release the healing material which then reacts with an embedded catalyst causing the polymerization reaction. Such a polymerization reaction may result in complete or partial repair or control of the cracked portion of the photoreceptor. Alternatively, in embodiments, when the catalyst can optionally be encapsulated in nano- or microcapsules. Thus, when the capsule ruptures, catalyst may be released and may then react with self-healing material.

[0057] In embodiments, the healing materials can undergo chemical reaction(s) or polymerization to form a polymer that heals cracks or other physical defects. For example, healing materials may include monomers or prepolymers capable of performing radical polymerization; monomers or prepolymers capable of performing hydrosilylation; monomers or prepolymers capable of performing Diels-Alder reaction; monomers or prepolymers capable of performing ring opening polymerization-radical, and the like. To facilitate the healing effect of the self-healing material, a corresponding catalyst or compound to facilitate the chemical reaction or polymerization may be also included.

[0058] Illustrative examples of healing materials may include, but not limited to:

i) unsaturated monomers or prepolymers capable of radical polymerization, such as acrylates, alkyl acrylates, styrenes, butadienes and the like; atom transfer radical polymerization catalyst system or radical initiator compound may be employed to facilitate healing effect; ii) room temperature vulcanizable ("RTV") silicone prepolymers, such as vinyl-containing polysiloxanes and hydrosiloxane-containing polysiloxanes, and the like; hydrosilylation initiator or catalyst, such as platinum catalyst, may be employed to facilitate healing effect; and iii) dienes and dienophiles capable of Diels-Alder reaction: such as furan and maleimide monomers or prepolymers, and the like; Lewis acid catalyst may be employed to facilitate healing effect. Optionally, heat may be applied to drive a retro-Diels-Alder reaction thereby regenerating the furan and maleimide monomers for repeated fracture-healing cycles. Additionally, lactones capable of ring opening polymerization to form polyesters, such as caprolactone, and the like; cyclic ester polymerization catalyst, such as scandium triflate; cyclic olefins capable of ring opening polymer-

ization: such as dicyclopentadienes (DCPD), substituted DCPD, norbornenes, substituted norbornenes, cyclooctadienes, and the like; and metathesis polymerisation (ROMP) catalyst, such as Grubbs' catalyst, may be employed to facilitate healing effect,

[0059] In embodiments, the polymer matrix 6 employed for the photoconductive coating may further comprises a reactive moiety 7 capable of reacting with the healing materials described herein to improve healing effects, such as adhesion and mechanical properties. Illustrative examples of such reactive moiety include vinyl, acrylic group, hydrosiloxane group, diene group, dielophile group, cyclic olefin group, and the like.

[0060] Nano- or microcapsule diameter and surface morphology may significantly affect capsule rupture behavior. The microcapsules may possess sufficient strength to remain intact during processing, yet rupture when the photoreceptor is damaged. In embodiments, the microcapsules may exhibit high bond strength to the photoreceptor materials, combined with a moderate strength microcapsule shell. In embodiments, the capsules may be impervious to leakage and diffusion of the encapsulated (liquid) healing material for considerable time in order to, for example, extend shelf life. In embodiments, these combined characteristics can be achieved, for example, with a system based on capsules with a suitable wall comprised of urea-formaldehyde resins, melamine formaldehyde resins, polyesters, polyurethanes, polyamides and the like.

[0061] There is significant scientific and patent literature on encapsulation techniques and processes. For example, microencapsulation is discussed in detail in "Microcapsule Processing and Technology" by Asaji Kondo, 1979, Marcel Dekker, Inc; "Microcapsules and Microencapsulation Techniques by Nuyes Data Corp., Park Ridge, N.J. 1976. Illustrative encapsulation includes chemical processes such as interfacial polymerization, in-situ polymerization, and matrix polymerization, and physical processes, such as centrifugal extrusion, phase separation, and core-shell encapsulation by vibration, and the like. Materials may be used for interfacial polymerization include, but not limited to, diacyl chlorides or isocyanates, in combination with di- or poly- alcohols, amines, polyester polyols, polyurea, and polyurethanes. Useful materials for in situ polymerization include, but not limited to, polyhydroxyamides, with aldehydes, melamine, or urea and formaldehyde, and the like.

[0062] In embodiments, the microcapsules are substantially spherical in shape and may have an average diameter of from 20 nanometers to about 250 nanometers, about 0.25 micrometer to about 5 micrometers, or from about 5 micrometers to about 20 micrometers. Microcapsules may comprise from about 70% to about 95% by weight of lubricant, such as from about 83% to about 92% by weight, or other fill material. Microcapsules may thus comprise about 5% to about 30% by weight of the total aggregate weight of the microcapsule and its fill

content, such as from about 8% to about 17%, or from about 1% to about 10%. Microcapsule shell wall thickness may be from about 10 nm to about 250nm, for example, from about 20 nm to about 200nm. Microcapsules in this range of shell thickness may be sufficiently robust to survive handling and manufacture, yet when embedded in an epoxy matrix, for example, the microcapsules may rupture and release their content at the site of damage. Nanoparticles of the microcapsule material may form on the surface of the microcapsules during production, thereby producing a rough surface morphology. Rough surface morphology may, for example, enhance mechanical adhesion when the microcapsules are embedded in a polymer, thus improving performance as a lubrication mechanism.

[0063] The following Examples are being submitted to illustrate embodiments of the present disclosure. These Examples are intended to be illustrative only, and are not intended to limit the scope of the present disclosure. Also, parts and percentages are by weight unless otherwise indicated. Comparative Examples and data are also provided.

[0064] Self healing layers of photoreceptors can be prepared by any conventional means or any other method obvious to those skilled in the art which would produce the desired overcoat layer.

[0065] An electrophotographic photoreceptor containing a self-lubricating layer was fabricated in the following manner. A coating solution for an undercoat layer comprising 100 parts of a zirconium compound (trade name: Organics ZC540), 10 parts of a silane compound (trade name: A110, manufactured by Nippon Unicar Co., Ltd), 400 parts of isopropanol solution and 200 parts of butanol was prepared. The coating solution was applied onto a cylindrical aluminum (Al) substrate subjected to honing treatment by dip coating, and dried by heating at 150 °C for 10 minutes to form an undercoat layer having a film thickness of 0.1 micrometer.

[0066] A 0.5 micron thick charge generating layer was subsequently dip coated on top of the undercoat layer from a dispersion of Type V hydroxygallium phthalocyanine (12 parts), alkylhydroxy gallium phthalocyanine (3 parts), and a vinyl chloride/vinyl acetate copolymer, VMCH (Mn = 27,000, about 86 weight percent of vinyl chloride, about 13 weight percent of vinyl acetate and about 1 weight percent of maleic acid) available from Dow Chemical (10 parts), in 475 parts of n-butylacetate.

[0067] Subsequently, a 25 μm thick charge transport layer (CTL) was dip coated on top of the charge generating layer from a solution of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (82.3 parts), 2.1 parts of 2,6-di-tert-butyl-4-methylphenol (BHT) from Aldrich and a polycarbonate, PCZ-400 [poly(4,4'-dihydroxydiphenyl-1,1'-cyclohexane), M_w = 40,000] available from Mitsubishi Gas Chemical Company, Ltd. (123.5 parts) in a mixture of 546 parts of tetrahydrofuran (THF) and 234 parts of monochlorobenzene. The CTL was dried at 115°C for 60 minutes.

[0068] On top of the charge transport layer, a self-healing overcoat layer was coated from a suspension comprising 1.5 parts of polyol (Joncryl 587, BASF, The Chemical Company), 2.4 parts of N,N'-diphenyl-N,N'-bis(3-hydroxyphenyl)-(1,1'-biphenyl)-4,4'-diamine as charge transport component, 2.1 parts of melamine resin (Cymel 303, Cytec Industries Inc.), 0.045 part of acid catalyst (Nacure 5225, King Industries Inc.), and 0.32 part of silicone oil capsules (average size: 5 microns, prepared by in situ polymerization from urea and formaldehyde) in 22 parts of Dowanol PM (Sigma Aldrich), followed by thermal curing at 140 °C for 40 minutes to form an overcoat layer having a film thickness of 5 μm. The resulted overcoat resin layer contained about 5 weight percent of the encapsulated healing material.

[0069] A Comparative Example photoreceptor or photoconductor was prepared by repeating the above process except that the overcoat layer was applied without the self-healing capsules.

[0070] Evaluation of Photoreceptor Performance Properties:

[0071] The electrical performance characteristics of the above prepared photoreceptors such as electrophotographic sensitivity and short term cycling stability were tested in a scanner. The scanner is known in the industry and equipped with means to rotate the drum while it is electrically charged and discharged. The charge on the photoconductor sample is monitored through use of electrostatic probes placed at precise positions around the circumference of the device. The photoreceptor devices are charged to a negative potential of 500 Volts. As the devices rotate, the initial charging potentials are measured by voltage probe 1. The photoconductor samples are then exposed to monochromatic radiation of known intensity, and the surface potential measured by voltage probes 2 and 3. Finally, the samples are exposed to an erase lamp of appropriate intensity and wavelength and any residual potential is measure by voltage probe 4. The process is repeated under the control of the scanner's computer, and the data is stored in the computer. The PIDC (photo induced discharge curve) is obtained by plotting the potentials at voltage probes 2 and 3 as a function of the light energy. The photoreceptor having the self-healing overcoat layer showed comparable PIDC characteristics as the control or Comparative Example device.

[0072] The electrical cycling performance of the photoreceptor was performed using a in-house fixture similar to a xerographic system. The photoreceptor device with the overcoat showed stable cycling of over 170,000 cycles in a humid environment (28 °C, 80%RH).

[0073] The torque properties, measured in Newton-meter, of the photoreceptor are measured in the following manner. A photoreceptor was placed in a xerographic customer replaceable unit (CRU), as is used in a DC555 (manufactured by Xerox Corporation). The average of the torque was measured at six seconds of rotation of the photoreceptor devices. The photoreceptor

with the self-lubricating overcoat layer disclosed herein possessed a torque value of 0.7 Newton-meter, which was about 25% lower than the comparative example device.

Claims

1. A photoconductive member comprised of a self-healing composite coating comprising a polymer matrix, a photoconductive component, a healing material encapsulated within nano- or microcapsules, and an optional catalyst, wherein said healing material is capable of repairing physical damage to the photoconductive member when the capsule ruptures.
2. The photoconductive member of claim 1, wherein the nano- or microcapsules comprise at least one of a healing material comprised of a monomer or an oligomer capable of performing polymerization, and a thin wall/shell, wherein said healing material is contained within the wall/shell.
3. The photoconductive member of claim 1, wherein said healing material is selected from the group consisting of olefins, cyclic olefins, lactones, acrylates, and organic silanes.
4. The photoconductive member of claim 1, wherein said thin wall/shell is comprised of a polymeric material selected from the group consisting of urea-formaldehyde resins, melamine formaldehyde resins, polyesters, and polyurethanes.
5. The photoconductive member of claim 1, wherein said catalyst is capable of accelerating the reaction of said healing material, and wherein the catalyst is present in the polymer matrix or on the surface of the capsules.
6. The photoconductive member of claim 1, wherein said catalyst comprises at least a member selected from the group consisting of transition metal catalysts, ROMP catalysts, and Lewis acid catalysts.
7. The photoconductive member of claim 1, wherein said healing material comprises cyclic olefins, and said catalyst comprises ROMP catalysts.
8. The photoconductive member of claim 1, wherein said polymer matrix further possesses a reactive group capable of reacting with the healing material.
9. The photoconductive member of claim 1, wherein said photoconductive component is a charge transport compound.
10. The photoconductive member of claim 1, wherein

said photoconductive component is comprised of a tertiary arylamine.

11. The photoconductive member of claim 1, wherein said photoconductive component comprises a photosensitive pigment. 5
12. The photoconductive member of claim 1, wherein said photoconductive component comprises a photosensitive pigment selected from the group consisting of a perylene pigment, an azo pigment, and a phthalocyanine pigment. 10
13. The photoconductive member of claim 1, wherein said photoconductive component is comprised of a semiconductive metal oxide. 15
14. A photoconductive member comprising a substrate, an undercoat layer, a charge generating layer, a charge transport layer, and an optional protective overcoat layer; 20
wherein at least one layer of said photoconductive member further comprises a healing material encapsulated within nano- or microcapsules and an optional catalyst, wherein said healing material is capable of repairing a physical damage of the photoconductive member when the capsule rupture. 25
15. An imaging forming apparatus comprising a charging device, a toner developer device, a cleaning device, and a photoreceptor comprising a conductive substrate, a charge generating layer, a charge transport layer, and an optional overcoat layer, wherein at least one layer of the photoreceptor contains healing material encapsulated within nano- or microcapsules and an optional catalyst. 30 35

40

45

50

55

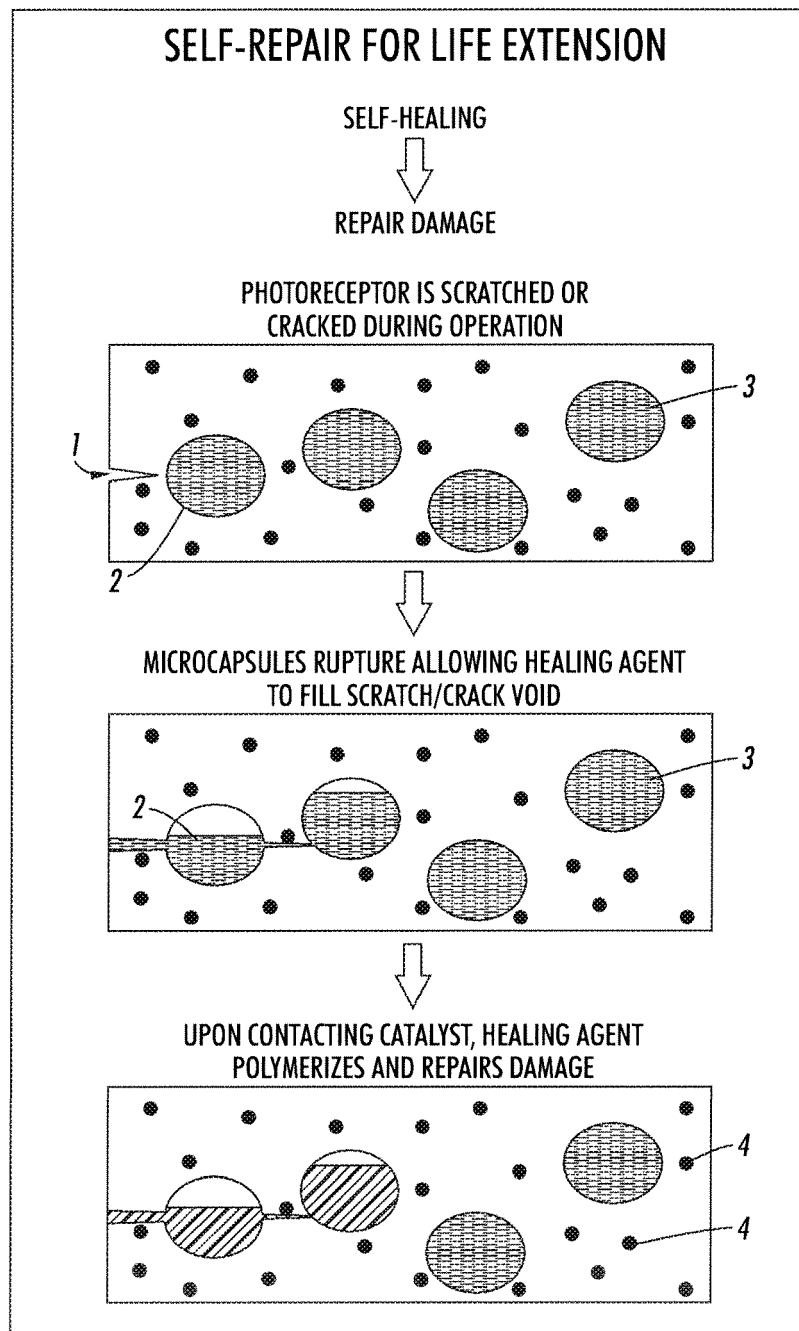
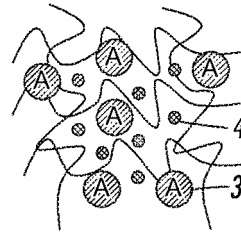


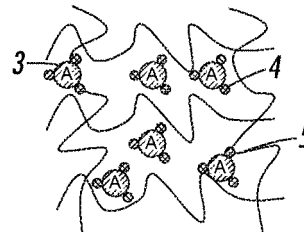
FIG. 1

FIG. 2(A)



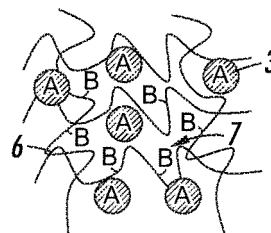
A: HEALING MATERIAL
 C: CATALYST OR ENCAPSULATED CATALYST

FIG. 2(B)



A: HEALING MATERIAL CAPSULE
 C: CATALYST COATED ON THE SURFACE OF
 HEALING MATERIAL CAPSULE

FIG. 2(C)



A: HEALING MATERIAL CAPSULE
 B: REACTIVE GROUP CHEMICALLY BOUND
 WITH POLYMER MATRIX
 (OPTIONALLY THE COATING FURTHER COMPRISES
 A CATALYST)



EUROPEAN SEARCH REPORT

Application Number
EP 09 15 2422

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	WO 2006/030618 A (FUJI ELECTRIC IMAGING DEVICE [JP]; NISHINA TSUTOMU [JP]; NAKAMURA YOIC) 23 March 2006 (2006-03-23) * the whole document *	1-15	INV. G03G5/047 G03G5/05 G03G5/06 G03G5/147
P	& US 2008/160438 A1 (NISHINA TSUTOMU [JP] ET AL) 3 July 2008 (2008-07-03) * paragraphs [0029], [0047]; claims *		
A	US 2006/286473 A1 (KAMI HIDETOSHI [JP]) 21 December 2006 (2006-12-21) * paragraphs [0012] - [0016], [0043] - [0047]; claims *	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			G03G
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		7 July 2009	Buscha, Andreas
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

1
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 09 15 2422

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

07-07-2009

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2006030618 A	23-03-2006	DE 112005001471 T5	04-10-2007
		JP 2006099035 A	13-04-2006
		KR 20070058446 A	08-06-2007
		US 2008160438 A1	03-07-2008

US 2008160438 A1	03-07-2008	DE 112005001471 T5	04-10-2007
		JP 2006099035 A	13-04-2006
		WO 2006030618 A1	23-03-2006
		KR 20070058446 A	08-06-2007

US 2006286473 A1	21-12-2006	JP 2006350163 A	28-12-2006

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- US 5702854 A [0002]
- US 5976744 A [0003]
- US 20070072101 A1 [0004]
- US 29513405 A [0005]
- US 20060105264 A1 [0006]
- US 4871634 A [0008]
- US 4457994 A [0009]
- US 4338387 A [0031]
- US 4286033 A [0031]
- US 4291110 A [0031]
- US 3121006 A [0039] [0046]
- US 23427505 A [0051]

Non-patent literature cited in the description

- Microcapsule Processing and Technology. Marcel Dekker, Inc, 1979 [0061]
- Microcapsules and Microencapsulation Techniques. Park Ridge, 1976 [0061]